

STUDY OF THE CHARACTERISTICS OF SOME SOLID-STATE
ANION MEMBRANE ELECTRODES IN RELATION TO THEIR
APPLICATIONS IN ANALYTICAL CHEMISTRY

THESE

présentée à la faculté des sciences
de l'Université de Genève
pour obtenir le grade de docteur ès sciences chimiques

par

Nalini PARTHASARATHY

de

Madras (Inde)

Texte condensé de la thèse No 1691 approuvée par la faculté des sciences.

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La Faculté des sciences, sur le préavis du professeur ordinaire Denys Monnier, directeur de thèse, et d'une Commission composés du professeur P. Lerch (EPF de Lausanne) et du chargé de recherche J. Buffle (Faculté des sciences), autorise l'impression de la présente thèse, sans exprimer d'opinion sur les propositions qui y sont énoncées.

Genève, le 24 février 1975

Le Doyen :

Thèse No 1691

Jean MULLER



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STUDY OF THE CHARACTERISTICS OF SOME SOLID-STATE ANION MEMBRANE ELECTRODES IN RELATION TO THEIR APPLICATIONS IN ANALYTICAL CHEMISTRY.

1. Introduction

The development of ion selective electrodes (I.S.E.) in recent years (1-4) has made a great impact on the analyst because these electrodes are both simple to use and allow rapid analytical determination.

However, in several cases these hopes have not been borne out for various reasons such as lack of selectivity, slow response time and insufficient sensitivity for direct measurement. These limitations arise from the inadequate knowledge of the behaviour of these electrodes. Thus, the aim of the present work has been to study the influence of various factors on the response of solid-state electrodes in particular the fluoride and the chloride electrodes so that they may be used under optimal conditions.

2. General principle

2.1. Important parameters

The potential, E_m , developed across the membrane of an ion selective electrode is given by the Nernst equation :

$$E_m = E^0 - 2.3 \cdot \frac{R.T}{n.F} \log a \quad (1)$$

where E^0 is the standard electrode potential, R, T, n and F have their usual meanings and a is the activity of the potential determining ion. At constant ionic strength the above expression can be written as :

$$E = E' - s \log c \quad (2)$$

where s is the electrode slope and is close to the nernstian value of

$$\frac{2.3 R T}{n.F}, \quad c \text{ is the concentration and}$$

$$E' = E^0 + s \log \gamma \quad (2')$$

where γ is the activity coefficient.

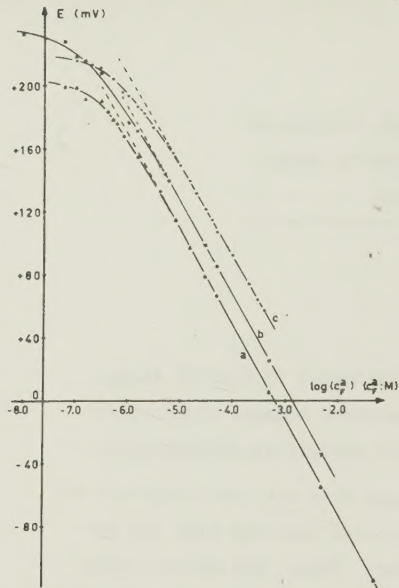


Fig. 1. Calibration curves for fluoride electrodes Beckman 39600 (curve c), Beckman 39650 (curve a), Orion 94-09A (curve b). The values of E' and s , obtained by least-squares fit are:

Curve	E' (mV)	s (mV)
a	-193.9	60.3
b	-170.3	59.2
c	-137.8	57.2

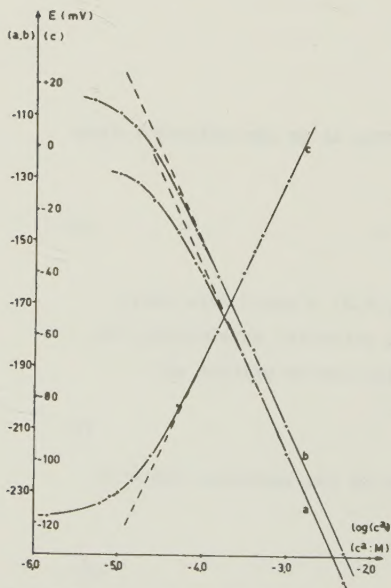


Fig. 2. Calibration curves for chloride electrode, using Cl^- (curve a, b) or Ag^+ (curve c) as potential-determining ion. The values for E' , s obtained by least-squares fit are:

Curve	E' (mV)	s (mV)	Ionic strength
a	-394.4	59.0	0.5 M
b	-382.7	58.2	10^{-2} M
c	+165.0	58.4	10^{-2} M

Preliminary studies with the fluoride and chloride electrodes showed that the equation (2) is obeyed in the concentration range 10^{-1} to 5.10^{-6} M for the former and in the concentration range 10^{-1} to 10^{-4} for chloride ions (see figures 1 and 2). The slopes of fluoride and chloride electrodes were found to be 59.2 and 59.0 respectively which are close to the nernstian value of 59.16 at 25°C. The cause for departure from linearity at low concentrations (see Figs 1 and 2) of test ions will be explained later.

2.2. Effect of pH on the response of fluoride electrode

The response of the electrode was found to be independent of pH in the pH range 4.5 to 7.0 for 10^{-4} M fluoride concentration but at pH greater than 7 hydroxide ions interfere and below pH 4.5 the hydrogen ions interfere due to the formation of HF. These findings are in accordance with those cited in the literature(4).

2.3. Sources of error in different methods of ion-analysis : application in fluoride analysis.

The determination of concentration of an ion using I.S.E. can be carried out by the following methods :

- 1) direct potentiometry
- 2) linear null point potentiometry
- 3) addition or Gran plot method

2.3.1. Direct reading method (5)

In this method a reference calibration curve is constructed (Figure 1) and the potential E of the solution under investigation is measured. The concentration corresponding to E is read from the calibration curve. E is also given by

$$E = E_j + E^o - E_{\text{ref.}}^{\text{ext.}} + s \log (c_T / \alpha) \quad (3)$$

where c_T is the total concentration of the test ion, α is the degree of complexation (ref.6) and is equal to c_T / c , where c is the free test ion concentration.

The disadvantages of this technique are :

- a) the necessity of constructing a calibration curve daily because of drift in E^0 value.
- b) information regarding the magnitude of α can not be obtained.

From equation (3), the error made in c , can be written as (7) :

$$\frac{\Delta c}{c} = \frac{\Delta S}{s^2} \underbrace{(E + E_{\text{ref}}^{\text{ext}} - E^0 - E_j)}_A + \frac{\Delta E}{s} + \underbrace{(E_{\text{ref}}^{\text{ext}} + E^0)}_B \frac{1}{s} + \underbrace{E_j / s + \Delta \gamma / \gamma}_D \quad (4)$$

where ΔE is the statistical error in E and ΔE^0 , $\Delta E_{\text{ref}}^{\text{ext}}$, ΔS and $\Delta \gamma$ are the variations in the measured values of respective parameters E^0 , E , $E_{\text{ref}}^{\text{ext}}$, γ and s .

The terms A, B and D in equation (4) were considered in turn to find out which of these terms contributes most to the error in c .

It was found that the error due to term A is negligible since the value of s does not change with time and can be determined fairly accurately. The error due to term B can be minimized by constructing a calibration curve daily. Hence the chief source of error arises from the term D which contains the activity coefficient parameter. A small difference in ionic strength (I.S.) between standard and sample solution will give rise to an appreciable error in concentration. A plot of relative error in γ against variation in I.S., for fluoride measurements with fluoride electrode is shown in Fig. 3. These results were obtained by measuring the potential of 10^{-4} M fluoride solution at a fixed ionic strength 0.1 M KNO_3 . Then the potential of sample solution of "known" concentration (10^{-4}) was measured for various concentrations of KNO_3 . $\Delta \gamma / \gamma$ was evaluated as follows :

$$\frac{\Delta \gamma}{\gamma} = 10 \frac{E - E_x}{s} - -1 = \frac{\gamma_x - \gamma}{\gamma} \quad (5)$$

where E is the potential of standard solution and E_x the potential of sample solution, γ and γ_x are the corresponding activity coefficients. These calculations were done assuming ΔE_j to be zero, which under the conditions used is a reasonable assumption, since the mobilities of the ions of the reference solution and the background electrolyte are nearly

the same. However, in practice ΔE_j will not be negligible, especially when the medium is complex in which case error due to ΔE_j has to be taken into account. The theoretical curve in fig. (3) (solid line) was obtained by using the values of the mean activity coefficients of $\bar{\gamma}_{KF}$, $\bar{\gamma}_{KCl}$ for KF and KCl given by Robinson and Stokes (8).

2.3.2. Linear null point potentiometry

In the linear null point potentiometry (9) the analate solution is placed in one half cell and the standard solution in the other half cell, and the concentration of the latter is adjusted such that potential difference between the two half cells is zero when measured with two identical I.S.E. The cell used is represented by :



The potential is given by :

$$E = E_1^0 - E_2^0 - E_{j,1} - E_{j,2} - \log \frac{(\gamma_1 c_1)^{s_1}}{(\gamma_2 c_2)^{s_2}} \quad (6)$$

where s_1 and s_2 are the electrodes slopes of I.S.E.₁ and I.S.E.₂ respectively. Other parameters are defined as before, the subscripts 1 and 2 refers to cell 1 and 2 respectively.

The concentrations of the unknown, under null point conditions is given by :

$$\log (c_1^{\text{T}} / \alpha) = s_2/s_1 \cdot \log \frac{c_2 \gamma_2}{(\gamma_1)^{s_1/s_2}} - s_2/s_1 \log \gamma_c + 2 \frac{\Delta E}{s_1} + \Delta E_j/j_1 \quad (7)$$

where ΔE is the statistical error in the null point measurement and $\Delta E_j = E_{j,1} - E_{j,2}$. Like the direct method, this method does not enable us to obtain the order of magnitude of α .

The error in c_1 can be computed from :

$$\frac{\Delta c_1}{c_1} = \frac{\Delta s}{s} \ln \left(\frac{c_2 \gamma_2}{\gamma_1} \cdot \frac{1}{\gamma_c} \right) + s_2/s_1 \cdot \Delta c_2 / c_2 + s_2/s_1 \cdot \frac{\Delta \gamma}{\gamma_1} + 2 \frac{\Delta E}{s_1} + \frac{\Delta E_j}{s_1} \quad (8)$$

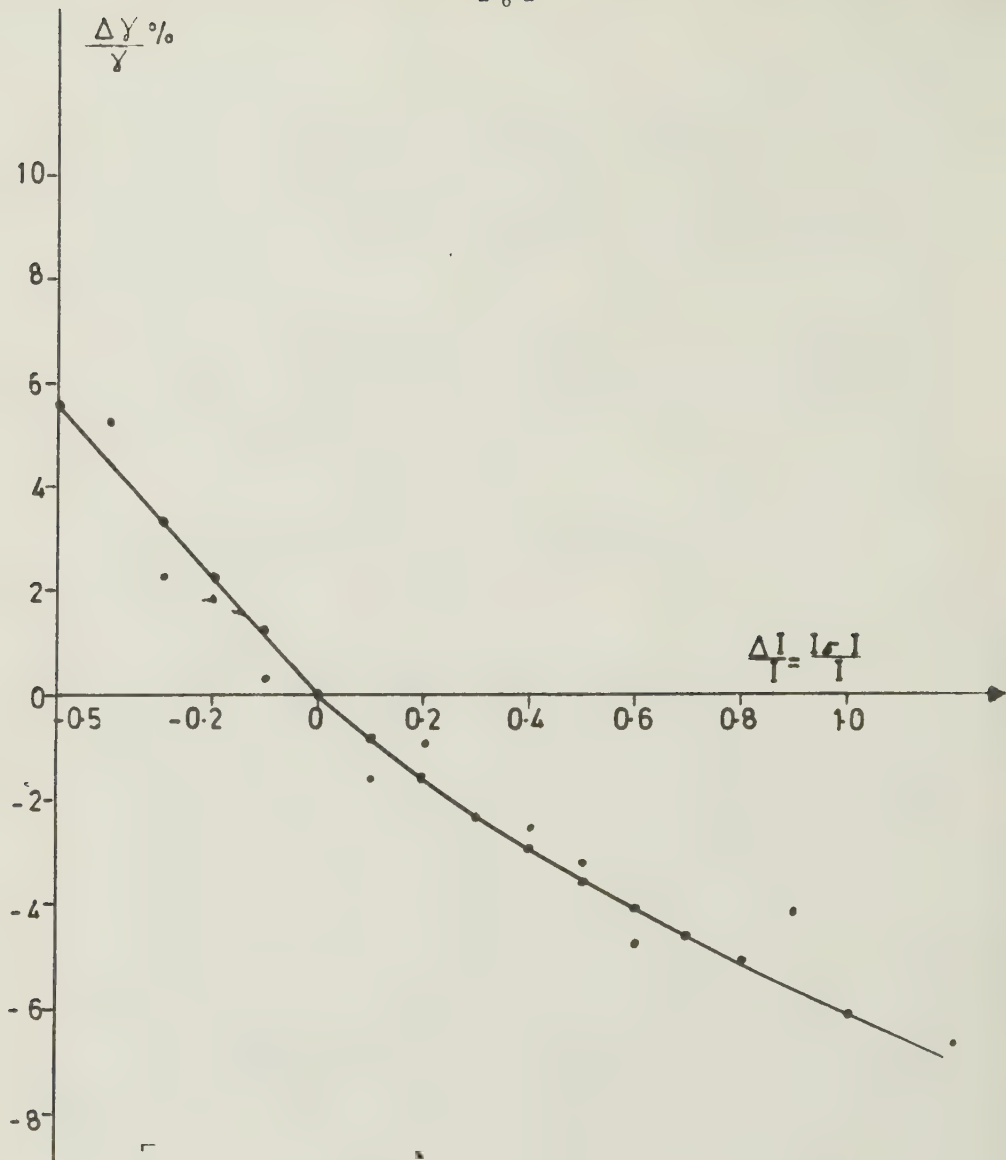


Fig. 7. Variation of activity coefficient of F^- as a function of change in ionic strength between the test soln. and standard soln. Background electrolyte = 1M KNO_3 .

The errors in E and c_2 are statistical errors whereas the errors in the other terms are systematic errors. Although the errors due to E^0 and E_{ref} are absent in this method, errors due to difference in slopes between the two electrodes and that due to c_2 are introduced instead ; the error incurred in the former parameter being appreciable and the latter being smaller than those made in E^0 and E_{ref} terms in the direct method (cf. eq 4). The error due to changes in ionic strength is of similar order of magnitude as the direct method.

2.4. Addition method or Gran plot method

2.4.1. Principle

In the addition technique (ref 10 11) the potential E_1 is measured for the sample solution of volume V_0 and total concentration c_0^T of the test ion. E_1 is given by :

$$E_1 = E' - s \log \frac{\gamma}{\alpha} (c_0^T + c_s) \quad (9)$$

where $E' = E^0 - E_{ref} - E_j$. The modified equation (cf. eq. 2) was found experimentally for fluoride electrode and this equation enables one to determine the concentration of unknown species even in the non linear portion of the calibration curve. c_s is a constant and equals to the difference between the observed concentration (assuming eq. 1) and the actual concentration used. This equation seems to be valid for other solid state electrodes such as Cu^{++} , Pb^{++} and Cd^{++} ; In the case of chloride electrode, as we shall see later that c_s can be replaced by a term containing solubility product of silver chloride. If known volumes (V) of standard solution of concentration c are added to the sample solution and the corresponding potentials E measured after each addition, then one obtains :

$$E = E' - s \log \frac{\gamma}{\alpha} \frac{(c_0^T + c_s) V_0 + (c + c_s) V}{(V + V_0)} \quad (10)$$

Rearranging equation 10 one gets

$$(V + V_0) \exp(E/s') = \exp(E'/s'') \cdot \gamma/\alpha \cdot ((c_0^T + c_s) V_0 + (c + c_s) V) \quad (11)$$

where $s' = s / \ln 10$ (12)

This is of the form

$$Y = A.V + B \quad (13)$$

where

$$A = \gamma/\alpha \cdot \exp (E'/s') (c + c_s) \quad (14)$$

$$B = \gamma/\alpha \cdot \exp (E'/s') (c_o + c_s) V_o \quad (15)$$

A plot of Y versus V should give a straight line and from the intercept on the V axis (V_x) (fig. 4) the concentration c_o can be evaluated. c_o is given by

$$c_o = (-V_x/V_o) (c + c_s) - c_s \quad (16)$$

The advantages of using this method are :

- a) electrode calibrations is not necessary
- b) this method allows us to compute the total concentration together with the value of α .

The error calculation for eq. (16) gives (7) :

$$\frac{\Delta c_o}{c_o} = (1 - c_s/c_o) \cdot \frac{\Delta V_x}{V_x} + \frac{\Delta V_o}{V_o} + \frac{\Delta c}{c+c_s} + \frac{\Delta c_s}{c_o} \quad (17)$$

Experimentally it was found that the principal source of error in the above expression arises from V_x term which is obtained by extrapolation. The extrapolation can be done statistically or graphically. The error in V_x consists of two parts viz. those stemming from the nature of the medium used e.g. ΔE_j and $\Delta \gamma$, and those arising from the experimental conditions used e.g. ΔV_x , ΔV_o , ΔE_o , c_o , V_o , N and V_{max} , where V_{max} is the maximum volume of standard solution added to the test ion solution and N is the number of addition.

The errors arising from E_j and I.S. variations should result in the departure from linearity in the Y vs V plot but results obtained with fluoride electrode showed that such deviations are observed only for I.S. above 3M. However, the extrapolated value of these plots lead to large error in c_o^T . The relative error in V_x as a function of I.S. is shown in fig. 5 .

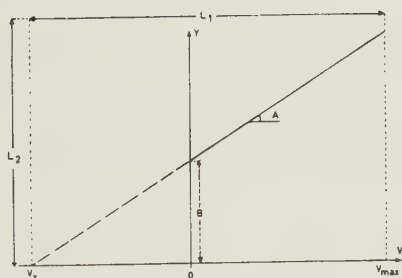


Fig. 1. Function $Y=f(V)$ and related parameters.

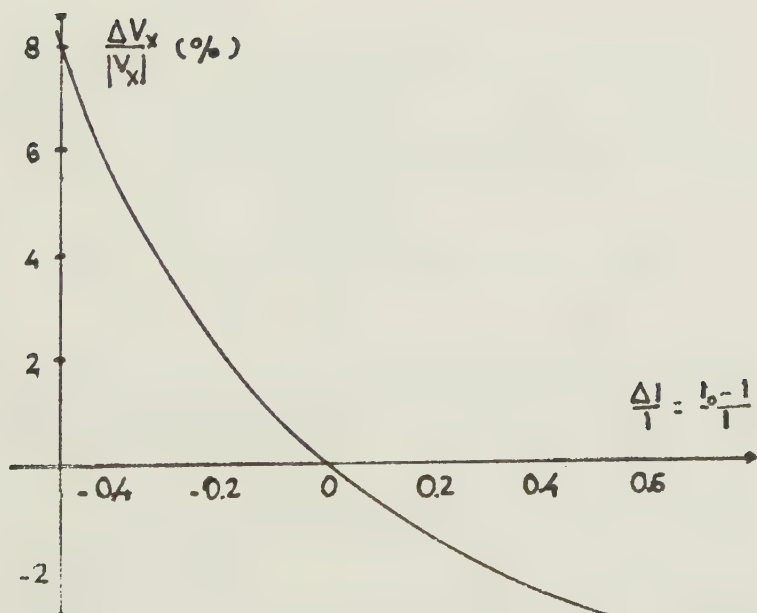


Fig. 2. Relative error in V_x as a function of varying ionic strengths between test soln. (I_0) and standard soln. (I).

Since the precision of the method depends on the experimental conditions used as stated above, titration conditions under which maximum precision i.e. $\Delta V_x / V_x$ is minimum, can be achieved was calculated theoretically for both statistical and graphical methods of extrapolation, and the results were verified experimentally with a fluoride electrode.

2. 4. 2. Theoretical calculation of $\Delta V_x / V_x$

2.4.2.1. Statistical error

For the calculation of $\Delta V_x / V_x$ the following symbols are used

$$V_i = i. V \quad V_{\max} = N.V.$$

Y_i = value of Y corresponding to V_i

$i = 1, 2, 3, \dots, N$

V and E are assumed to be independent random variables. This assumption is discussed in ref. (13). On this basis the first order linear regression was applied to the relation $Y_i = f(V_i)$, without going into the mathematical derivation, the relative error in V_x , $\Delta V_x / V_x$, is given by (12)

$$\frac{V_x}{V_x} = \frac{K}{B(1-k^2)^0} \cdot \left\{ \frac{1}{N} \cdot A^2(1-K^2) \cdot S_v^2 + y_m^2 \right\}^{\frac{1}{2}} \quad (18)$$

where $K = t_{\delta} \cdot \sigma_{A/A}$

The term δ is given by student distribution and the value of probability $\frac{A_{\exp} - A}{A} > t_{\delta}$, where $A_{\exp}$ is equal to the value of A determined experimentally and δ is the probability.

σ_A is the standard deviation of the slope A(ref. 11). Equation (18) was obtained for $\delta = 5\%$. σ and Y_m are standard deviation and mean value of Y and are defined as in classical statistics (ref 13).

In equation 10, if the constants E_o , s and c_s are known for a given ion selective electrode and values for c, c_o , V_o , $V_{\max}$, and N are chosen arbitrarily, then the value of Y_j can be calculated from equations 10, 11 and 12 and $\Delta V_x / V_x$ from equation 18.

2.4.2.2. Graphical method

In this method the factors regarding the dimensions L_1 and L_2 of the graph paper (Fig. 4), the error made on plotting and the error in reading V_x , must be considered. If L_1 is taken as unity, the following transformation can be brought about,

$$V_i = \frac{V_i}{V_{\max} - V} \quad \text{and} \quad Y_i = \frac{r_L}{Y_N}$$

where

$$r_L = \frac{L_2}{L_1}$$

The line $Y = f(V)$ can be expressed as

$$Y = P.V + q$$

where $P = A.r_L \frac{(V_{\max} - V_x)}{Y_N}$ and $q = B. \frac{r_L}{Y_N}$

using these expressions, and $\delta = 0.05$, the relative error in V_x is given by :

$$\begin{aligned} \frac{\Delta V_x}{V_x} &= \frac{\Delta V_x}{V_x} = \frac{(\sigma_{V_x}^2 + (\sigma_V)_1^2)^{\frac{1}{2}}}{V_x / (V_{\max} - V_x)} = \\ &= (1 + A \cdot \frac{V_{\max}}{B}) (\sigma_{V_x}^2 + (\sigma_V)_1^2)^{\frac{1}{2}} \end{aligned}$$

where $(\sigma_{V_x})_1$ is the error in reading the scale while reading the value of V_x on the graph and σ_{V_x} is the standard deviation in V_x .

2.4.3. Evaluation of the influence of different parameters on $\Delta V_x / V_x$

2.4.3.1. Statistical method

Theoretical calculations have shown that the error in V_x , $\Delta V_x / V_x$ depends both on the ratio $(c + c_s) / (c_o + c_s)$ and $V_{\max} / V_o$, and the minimum error in V_x ($\Delta V_x / V_x$) min, for given values of N , occurs for a certain values of R , $R_{\min}$, where

$$R_{\min} = \frac{(c + c_s)}{c_o + c_s} \cdot \frac{V_{\max}}{V_o} \quad (\text{see fig. 6})$$

2.4.3. Evaluation of the influence of different parameters on $\Delta V_x/V_x$

2.4.3.1. Statistical method of extrapolation

Theoretical calculations have shown that the error in V_x , $\Delta V_x/V_x$ depends both on the ratio $(c + c_s)/(c_o + c_s)$ and $V_{\max}/V_o$, and that the minimum error in V_x ($\Delta V_x/V_x$)_{min}, for given values of N , occurs for a certain value of R , $R_{\min}$, where

$$R_{\min} = \frac{c + c_s}{c_o + c_s} \cdot \frac{V_{\max}}{V_o} \quad (\text{see figure 6})$$

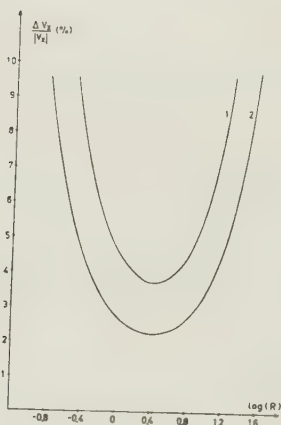


Figure No. 6 A graph of $\frac{\Delta V_x}{V_x}$ versus log. R for statistical method.

Symbols used for calculations are : $\sigma_{V_o/V_o} = 0.1\%$;
 $\sigma_{V/V} = 0.05\%$; $\sigma_E = 0.1$ mV ; $N = 10$; $V_{\max} = 10$ ml.

The curves do not depend on the value of C_o (1)

$V_o = 1$ ml and (2) $V_o > 10$ ml.

$(\Delta V_x/V_x)_{\min}$ and $R_{\min}$ depend on σ_V , σ_{V_o} and E . By keeping the parameters σ_{V/V_o} and σ_E constant and varying N , $V_{\max}$, V_o , c and c_o , successively, the calculation of $(\Delta V_x/V_x)_{\min}$ shows that for $V_{\max}/V_o < 2.5$ and $c/c_o > 1$ (if $c_s = 0$), $(\Delta V_x/V_x)_{\min}$ can be considered to be independent of both c/c_o and $V_{\max}/V_o$. On the other hand, it was found that for $\Delta V_x/V_x$ to be small, N should be greater than 10. Under these conditions, the value of

$R_{\min}$ can be considered to be independent of $V_{\max}/V_o$, c/c_o and N , and to depend only on the errors in V , V_o and E .

2.4.3.2. Appraisal of errors for graphical method of extrapolation

Graphical method gave similar results to those obtained by statistical method, with a minimum in the $(\Delta V_x/V_x)_{\min}$ Vs $\log R_{\min}$ plot. Because of the additional error incurred in reading the graph, the value of $R_{\min}$ and $(\Delta V_x/V_x)_{\min}$ differ in the two methods. However, it was seen that the relationship between the two sets of variables $R_{\min}$ and $(\Delta V_x/V_x)_{\min}$ on the one hand and N , C_o , V_o , $V_{\max}$ on the other are analogous to those obtained in the statistical method.

2.4.3.2. Influence of error in V , V_o , E , L_1 and L_2 on statistical error $(\Delta V_x/V_x)_{\min}$

From the above results, one would expect the results from both the methods to be identical when $(\sigma_Y)_1 = (\sigma_X)_1 = 0$. This was indeed found to be so, thus confirming the predictions made above. Thus from these results, it can be seen that theoretical optimal conditions are obtained when the following conditions are satisfied :

- 1) The value of R should lie between 1 and 3 ($R = c/c_o \cdot V_{\max}/V_o$), irrespective of the method used for extrapolation.
- 2) The number of addition N should be greater than 10.

Although either method can be used for extrapolation, the graphical method seems preferable for the application in unknown medium, because in that case, any non linearity in the Y vs V curve can be observed, whilst it may pass undetected in the statistical method. This non linearity appears when there is an interaction of the ion with the medium or when the electrode response is slow.

The effect of error in the electrode slopes on V_x was not considered in the foregoing discussion. It must be borne in mind that linearity in $Y = f(V)$ plot does not exclude the possibility of systematic errors owing to ionic strength changes as discussed earlier. Systematic error incurred in the electrode slope does not either affect the linearity, unless this error is very large.

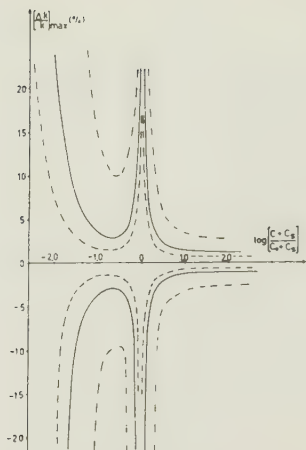


Fig. 1. The influence of titration conditions on the maximum value of $\Delta k/k$, $\langle \Delta k/k \rangle_{\max}$, for which the systematic error in V_e is not significantly greater than the statistical error. Calculations were performed for $R = 2.7$. (---) $N = 5$; (—) $N = 10$; (—) $N = 20$.

Fig. 2. The influence of titration conditions on the maximum value of $\Delta k/k$, $\langle \Delta k/k \rangle_{\max}$, for which the relation $Y = f(V)$ does not significantly deviate from linearity. Calculations were performed for $R = 2.7$. (---) $N = 5$; (—) $N = 10$; (—) $N = 20$.

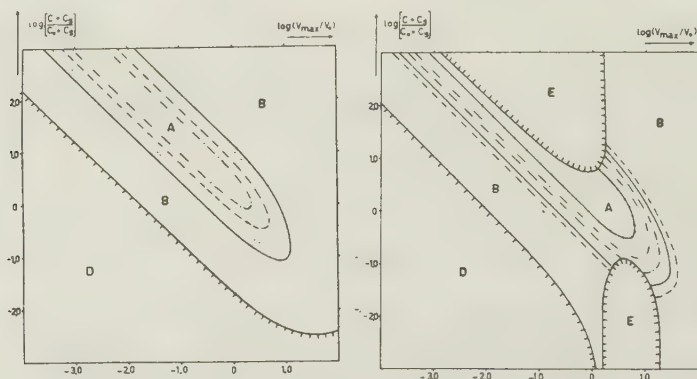


Fig. 3. The influence of titration conditions on $\Delta V_e/V_e$. Calculations were done using $N = 5$, $s_V/V_0 = 0.05\%$, $s_{V_0}/V_0 = 0.1\%$, $\Delta E = 0.1 \text{ mV}$, $\Delta k/k = 0$. A = region where $4 < \Delta V_e/V_e < 5$. B = region where $\Delta V_e/V_e > 10$. D = region where the slope of the regression line $Y = f(V)$ is not significantly different from 0. (—) $\Delta V_e/V_e = 10\%$; (.....) $\Delta V_e/V_e = 8\%$; (—) $\Delta V_e/V_e = 6\%$; (---) $\Delta V_e/V_e = 5\%$.

Fig. 5. Influence of titration conditions on $\Delta V_e/V_e$. $N = 10$, $\Delta k/k = +3.9\%$. A = region where $2 < \Delta V_e/V_e < 3$. B = region where $\Delta V_e/V_e < 9$. E = region where systematic error in V_e differs significantly from the statistical error. C = region where the deviation from linearity is significant for the relation $Y = f(V)$. (---) $\Delta V_e/V_e = 9\%$; (—) $\Delta V_e/V_e = 7\%$; (.....) $\Delta V_e/V_e = 6\%$; (---) $\Delta V_e/V_e = 5\%$; (—) $\Delta V_e/V_e = 4\%$; (+ + +) $\Delta V_e/V_e = 3\%$. All other conditions and definitions used are identical to those in Fig. 3.

2.4.3.3. Systematic error

Theoretical calculations in the preceeding section were carried out by assuming that the electrode slope is known with great accuracy. However, the electrode slope is obtained experimentally and the error incurred in s , Δs , causes a systematic error in V_x . Hence theoretical calculations were done to find out the part played by Δs in the determination of V_x .

The results of these calculations can be summarized as follows :

- a) For $c = c_o$, the plot of $Y = f(V)$ will yield different slopes and intercept on the ordinate but the intercept on the V axis will be identical. Under these conditions, the precision of V_x is independent of the error in s .
- b) For $c \neq c_o$, the greater the V_i/V_o ratio, the lesser will be the influence of s on V_x . The error in V_x provoked by s arises due to two factors viz. extrapolation error, i.e., the intercept on the V axis will be different from the expected value, and that due to non-linearity in the $Y = f(V)$ plot.

The quantitative evaluation of these two effects were carried out using $\gamma = \alpha = 1$, $s = 39.68 \text{ mV}^{-1}$ and $E'_o = 0.18 \text{ V}$. The values of the maximum relative errors, $(\Delta s/s)_{\text{max}}$, for extrapolation error, and $(\Delta s/s)_c$ for non-linearity error, as a function of $\log c/c_o$, were computed by putting $R = R_{\text{min}} = c/c_o$. $V_{\text{max}}/V_o = 2.7$. The results are illustrated in Figures 7 and 8. It can be seen that the extrapolation error always precedes the non-linearity error irrespective of the titration conditions. When ' s ' is positive, deviation from linearity is observed for $\Delta s/s > 100\%$, a condition never encountered in practice, Therefore, no indication of error in ' s ' would be given by merely examining the $Y = f(V)$ curve. Further, when $\Delta s = 0$, it was seen that $(c + c_s)/(c_o + c_s)$ and V_{max}/V_o behave as independent variables, regardless of the actual values of c , c_o , V_{max} and V_o . Hence, it is possible to calculate $\Delta V_x/V_x$ contours as a function of $\log (c + c_s)/(c_o + c_s)$ and V_{max}/V_o (Fig. 9 shows these curves). When $\Delta s \neq 0$, a plot of $\Delta V_x/V_x$, where V_x is the extrapolated value of V_x when $s \neq 0$, as a function of $\log (c + c_s)/(c_o + c_s)$ and V_{max}/V_o , yields curves as shown in Fig. 10. From this figure, it is apparent that the extrapolation error is detected before non-linearity error.

2.4.4. Experimental determination of errors in the gran plot method

In order to test the theory, experiments were performed with a fluoride electrode.

2.4.4.1. Experimental determination of statistical error in V_x

The results obtained for sample solutions of concentration 10^{-4} M fluoride ions under various experimental conditions are tabulated in Table 1. The value 's' used for determination of V_x was calculated by least square method for each titration. The regression line $Y = f(V)$ was calculated by using weighting factor and $\Delta V_x / V_x$ was evaluated from the variability of the slope of this line. A plot of $\log \Delta V_x / V_x$ versus $\log R$ (fig. 11) shows that the experimental curve has the same form as predicted by the theory but is slightly displaced from the theoretical curve. This difference arises because in the theoretical calculations σ_E , the error in E was assumed to be constant. In practice, this assumption may not be true. The change in E when c is close to c_0 is small, whereas when c differs considerably from c_0 , the change in E is large and σ_E is probably also larger than in the first case.

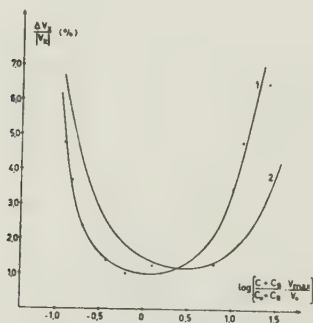


Figure 11 Relationship between statistical error in V_x , $\Delta V_x / V_x$, and the titration conditions.

$c_0 = 10^{-4}$ M, $V_0 = 40$ ml, $V_{\max} = 10$ ml, $N = 21$,

$\sigma_{V_0/V_0} = 0.1\%$, $\sigma_{V/V_0} = 0.025\%$, $\sigma_E = 0.05$ mV.

- (i) Experimental curve obtained by statistical extrapolation by using weighting factor.
- (ii) Theoretical curve evaluated for the same titration conditions.

2.4.4.2. Comparison of statistical and graphical methods of extrapolation

COMPARISON OF STATISTICAL AND GRAPHICAL METHODS OF EXTRAPOLATION FOR DIFFERENT C_0 RATIOS

($C_0 = 10^{-4}$ M, $V_0 = 40$ ml, $V_{max} = 10$ ml, $N = 20$: A = Statistical results with the weighting factor, B = statistical results without the weighting factor, C = graphical determination)

Titration no.	A		B		C
	V_x (ml)	$\Delta V_x / V_x$ (%)	V_x (ml)	$\Delta V_x / V_x$ (%)	V_x (ml)
$C/C_0 = 100$					
1	0.41	12.6	0.36	7.3	0.37
2	0.42	9.8	0.34	16.3	0.31
3	0.42	4.3	0.42	6.7	0.40
4	0.41	11.9	0.38	16.1	0.33
5	0.41	7.3	0.36	11.5	0.35
6	0.41	12.3	0.32	13.6	0.33
7	0.40	10.9	0.33	11.6	0.40
8	0.41	5.6	0.36	6.4	0.35
$C/C_0 = 5$					
1	8.01	0.98	7.95	1.23	8.04
2	8.03	1.03	7.98	1.09	8.00
3	8.03	1.1	7.96	1.12	8.07
4	8.30	1.2	8.23	1.2	8.24
5	8.05	1.5	8.00	1.5	8.11
6	8.27	1.3	8.32	1.4	8.37
7	7.96	1.01	7.92	1.01	7.93
8	7.96	0.79	7.93	0.84	7.9
9	8.0	0.96	7.98	1.29	8.04
$C/C_0 = 1$					
1	39.94	1.4	39.96	<0.01	40.3
2	40.00	<0.01	40.00	<0.01	39.6
3	40.00	<0.01	40.00	<0.01	39.96
4	40.00	<0.01	40.00	<0.01	39.6
5	40.95	0.9	40.03	0.97	41.22
6	40.00	<0.01	40.00	<0.01	39.96
7	40.00	<0.01	40.00	<0.01	39.8
8	40.00	<0.01	40.00	<0.01	39.9
9	40.43	0.7	40.36	0.7	40.5
10	40.00	<0.01	40.00	<0.01	39.96

The results of titration for three different concentrations of standard solutions are given in table 1 above. From the results, it can be seen that when c is not considerably different from c_0 ($c/c_0 = 5$ or 1), the graphical and least square fit methods are in good agreement. However, when c differs considerably from c_0 (i.e. $c/c_0 = 100$), either graphical or the least square fit without the weighting factor can lead to important error in the determination of C_x . Hence, in that case, the graphical method is not applicable, but it is possible to use the statistical method provided that a correct weighting factor can be determined.

2.4.4.3. Effect of systematic error on s , Δs

Experimentally it was found that the non-linearity in Y vs V plot occurs at very negative values of Δs , conditions which are hardly encountered in practice. Also, V'_x was found to increase with algebraic increase in s . The relative error in V_x for three titration conditions ($\log R = 0.6, 0.097$ and -0.21) were calculated and plotted against $\Delta s/s$ (Fig. 12). The values of $\Delta s/s$ were chosen arbitrarily. As can be seen, a small error in ' s ' causes a significant error in V_x and as it was also shown theoretically, a systematic error in V'_x can be produced even when the relation $Y = f(V)$ is linear. It should be noted that curve in Fig. 12 does not pass through the origin presumably because c/c_0 is high ($c/c_0 = 15$). As it was discussed previously, that for high c/c_0 ratios the graphical method produces the same type of error as statistical method without weighting factor, this error has to be added to the systematic error caused by Δs .

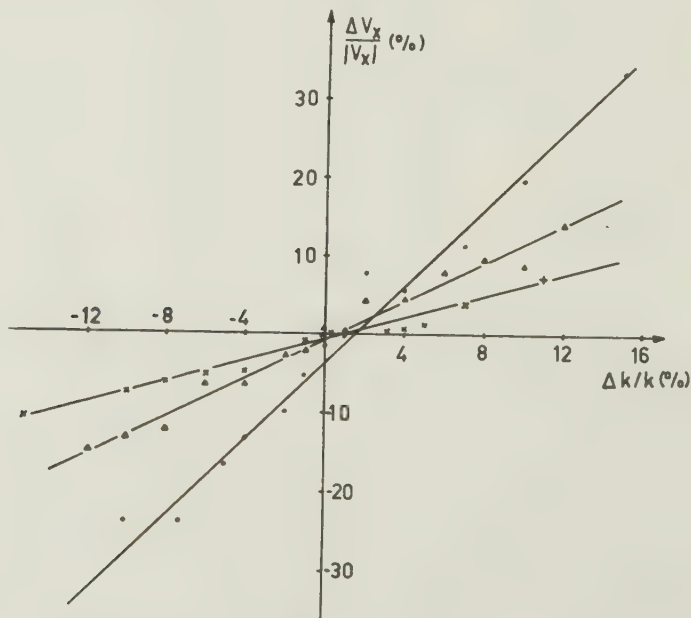


Figure 12

The variation of $\frac{\Delta V_x}{V_x}$ made in V_x obtained by graphical extrapolation as a function of error in s_0 , $c_0 = 10^{-4}$ M, $V_0 = 10$ ml, $V_{\max} = 10$ ml.

- (1) $c = 1.5 \cdot 10^{-3}$ M (o)
- (2) $c = 5.0 \cdot 10^{-4}$ M (Δ)
- (3) $c = 2.5 \cdot 10^{-4}$ M (x)

2.4.4.4. Conclusion

Error calculations in Gran Plot method have shown that optimal conditions are obtained when :

- 1) The value of R is between 1 and 3 ($R = c/c_o \cdot V_{\max}/V$) .
- 2) The number of addition N should be greater than 10.
- 3) The concentration of standard solution should be as close as possible to that of the unknown solution.
- 4) The electrode slope must be determined with utmost precision, under these conditions the precision in this method is better than the other two methods discussed.

3. Limitation of the sensitivity

In Section 2.1., it was pointed out that fluoride and chloride electrodes show non-nernstian behaviour below concentrations of about $5 \cdot 10^{-6}$ M and 10^{-4} M of the appropriate ions. Most of the solid state electrodes (e.g. Cu, Pb, Cd, etc.) show such a behaviour and various hypotheses have been laid to explain this discrepancy without actually making systematic studies confirming these hypotheses. However, sometimes it is essential to know the exact nature of the phenomenon limiting the sensitivity e.g. in the direct determination of solubility of inorganic salts. Hence, an attempt was made to look into the cause for the observed deviation. The most commonly cited factors for anomalous behaviour of I.S.E. (14 - 17) are the following :

- 1) The solubility of the electrode membrane
- 2) The presence of impurities of test ion in the background electrolyte
- 3) Adsorption of the test ions on the walls of the container.

3.1. Role of the solubility of the membrane

3.1.1. Theory

The response of anion selective electrode can be written as :

$$E = E' - s \log c_A \quad (21)$$

where c_A is the concentration of the anion under investigation.

Similarly for cation selective electrode :

$$E = E' + s \log c_M \quad (22)$$

where c_M = concentration of the metal ion.

The concentration c_A (or c_M) is the sum of two terms: the concentration of the anion added c_A^a and that arising from the dissolution of the electrode crystal c_A^d . Hence, we have

$$c_A = c_A^a + c_A^d \quad (23)$$

c_A^d can be expressed in terms of the solubility product of the crystal $A_{Z_M} M_{Z_A}$

$$c_A = c_A^a + \frac{Z_M}{Z_A} \cdot \frac{(K_{sp})^{Z_A}}{Y_M \cdot (Y_A)^{Z_M/Z_A}} \cdot \frac{1}{(c_A)^{Z_M/Z_A}} \quad (24)$$

where Z_M and Z_A are charges of cation M and anion A respectively. From this equation it can be seen that when c_A^a is very large, the second term on the right hand side (RHS) of the equation can be neglected. In this case, we have $c_A = c_A^a$ and this condition corresponds to the linear portion of the calibration curve (Figs. 1 and 2). On the other hand, for low concentration of c_A^a , the second term in eq (24) is no longer negligible and under these conditions it is possible to verify whether dissolution alone will account for the deviations observed on the experimental curve. This can be done by computing Δc_A where

$$\Delta c_A = c_A - c_A^a$$

c_A can be computed from equation (21) since E_1 , E' and s are known. Rewriting equation (24), one obtains :

$$c_A = c_A^a - c_A^a = \frac{Z_M}{Z_A} \cdot \frac{(K_{sp})^{Z_A}}{(Y_A)^{Z_A/Z_M}} \cdot \frac{1}{(c_A)^{Z_M/Z_A}} \quad (25)$$

Thus, a plot of c_A versus $\frac{1}{(c_A)^{Z_M/Z_A}}$ should give a straight line passing through the origin and from the slope the value of K_{sp} can be evaluated. Expression analogous to eq. (25) can also be obtained for electrodes responding to cations. Since measurements are made in the concentration range where errors in the measurement of c_A may be large, the order of magnitude of these errors were estimated by classical methods. The maximum systematic errors were estimated by classical methods. The maximum systematic errors in

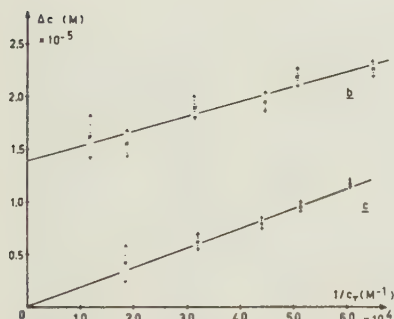
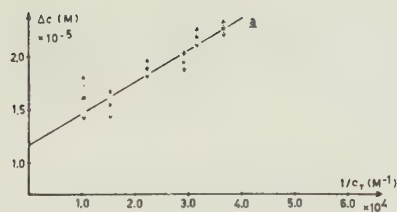


Fig. 3. Curves $\Delta c = f(1/c_T)$ obtained with chloride Beckman electrode, by using chloride as potential-determining ion. <.....> estimated error

Curve	Values on the abscissa	Electrolyte	Slope	Intercept on the ordinate
a	$1/c_T$	0.5 M NaNO ₃	$(3.0 \pm 0.4) \cdot 10^{-10}$	$(1.2 \pm 0.4) \cdot 10^{-5}$
b	$1/c_T - 1.2 \cdot 10^{-5}$	0.5 M NaNO ₃	$(1.3 \pm 0.6) \cdot 10^{-10}$	$(1.4 \pm 0.4) \cdot 10^{-5}$
c	$1/c_T$	10^{-2} M NaNO ₃	$(1.9 \pm 0.4) \cdot 10^{-10}$	0

Fisher coefficients corresponding to the hypothesis slope=0 and intercept on the ordinate=0, with 95% probability, are as follows:

Curve	Fisher coefficients		
	Calculated for slope	Calculated for intercept on the ordinate	Theoretical
a	37.32	58.8	7.71
b	34.79	141.85	7.71
c	188.29	0.005	10.13

c_A due to errors in 'E' and 's' were found to be 6% and 7% respectively, Hence, E' and S should be determined for each set of values in order to minimize the errors due to these parameters. In addition to this, statistical errors in c_A will be incurred due to statistical error on c_A^a (estimated to be 1.5 % for 10^{-5} and 2% for 10^{-7}).

3.1.2. Results with chloride electrode

From the plot of Δc_A against $1/c_A$ (Fig. 13), it is seen that a straight line is obtained which does not pass through the origin. This could be due to either the presence of impurities in the background electrolyte or interference of nitrate ion. From the slope of the line K_{sp} was found to be $(3.0 \pm 0.4) \times 10^{-10}$ M and the intercept on the 'Y' axis = $(1.2 \pm .4) 10^{-5}$ M. Moreover, the concentration of silver (I) ions found by A.AS in solutions of low concentrations of chloride ions which had been pre-equilibrated with the electrode confirmed that chloride impurities or interference of the background electrolyte gives rise to the constant term obtained in the plot in Fig. (13) (curve 2a).

3.1.3. Role of impurities or interferences

In addition to the solubility, the presence of test ions as impurities in the background electrolyte used or interference of nitrate ions could contribute to the total concentration of chloride ions in the sample solution. This would imply that the contribution of the latter parameters would be negligible if measurements are made at low concentration of background electrolyte. This was indeed found to be so confirming that the impurities or interference play some part at low concentrations of test ions. The value of solubility product in this case was found to be $1.9 \cdot 10^{-4}$ ($I = 0.01$ MK NO_3) which is in agreement with that given in the literature (18). The same results were obtained with the usage of silver (I) ion as the 'test ion'. Thus, solubility seems to be the factor limiting the sensitivity of chloride electrode.

3.2. Results obtained with fluoride electrode

The values of c_A^a , c_F and Δc_F calculated from fig. (1) for three fluoride electrodes are given in Table II. It is seen that Δc_F is practically independent of c_F consequently the solubility product calculated from eq. (24)

varies with c_F^a (see col. 4 of Table II). Hence, solubility alone is inadequate in explaining the anomalous behaviour of fluoride electrode.

Table II

Values of Δc_F for various fluoride electrodes

$c_F^a (M)$	$c_F (M)$	$\Delta c_F (M)$	Apparent solubility product (from eqn. 5)
<i>Beckman electrode 39600</i>			
$3.00 \cdot 10^{-6}$	$3.63 \cdot 10^{-6}$	$6.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-23}$
$2.00 \cdot 10^{-6}$	$2.54 \cdot 10^{-6}$	$5.4 \cdot 10^{-7}$	$2.9 \cdot 10^{-24}$
$1.50 \cdot 10^{-6}$	$2.14 \cdot 10^{-6}$	$6.4 \cdot 10^{-7}$	$1.7 \cdot 10^{-24}$
$1.00 \cdot 10^{-6}$	$1.62 \cdot 10^{-6}$	$6.2 \cdot 10^{-7}$	$8.8 \cdot 10^{-25}$
$7.50 \cdot 10^{-7}$	$1.44 \cdot 10^{-6}$	$6.9 \cdot 10^{-7}$	$4.8 \cdot 10^{-25}$
$3.00 \cdot 10^{-7}$	$7.96 \cdot 10^{-7}$	$5.0 \cdot 10^{-7}$	$8.3 \cdot 10^{-26}$
$2.00 \cdot 10^{-7}$	$7.24 \cdot 10^{-7}$	$5.2 \cdot 10^{-7}$	$6.6 \cdot 10^{-26}$
$1.00 \cdot 10^{-7}$	$6.33 \cdot 10^{-7}$	$5.3 \cdot 10^{-7}$	$4.5 \cdot 10^{-26}$
<i>Beckman combination electrode 39650</i>			
$1.50 \cdot 10^{-6}$	$1.66 \cdot 10^{-6}$	$1.6 \cdot 10^{-7}$	$2.4 \cdot 10^{-23}$
$8.00 \cdot 10^{-7}$	$9.85 \cdot 10^{-7}$	$1.9 \cdot 10^{-7}$	$5.9 \cdot 10^{-26}$
$6.00 \cdot 10^{-7}$	$7.20 \cdot 10^{-7}$	$1.2 \cdot 10^{-7}$	$1.5 \cdot 10^{-26}$
$5.00 \cdot 10^{-7}$	$6.62 \cdot 10^{-7}$	$1.6 \cdot 10^{-7}$	$1.6 \cdot 10^{-26}$
$4.00 \cdot 10^{-7}$	$5.50 \cdot 10^{-7}$	$1.5 \cdot 10^{-7}$	$8.3 \cdot 10^{-27}$
$3.00 \cdot 10^{-7}$	$4.27 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$	$3.3 \cdot 10^{-27}$
$1.50 \cdot 10^{-7}$	$4.05 \cdot 10^{-7}$	$2.6 \cdot 10^{-7}$	$5.6 \cdot 10^{-27}$
$1.00 \cdot 10^{-7}$	$3.00 \cdot 10^{-7}$	$2.0 \cdot 10^{-7}$	$1.8 \cdot 10^{-27}$
$6.00 \cdot 10^{-8}$	$2.98 \cdot 10^{-7}$	$2.4 \cdot 10^{-7}$	$2.1 \cdot 10^{-27}$
<i>Orion electrode 94-09 A</i>			
$3.00 \cdot 10^{-7}$	$4.25 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$	$3.2 \cdot 10^{-27}$
$1.50 \cdot 10^{-7}$	$3.00 \cdot 10^{-7}$	$1.5 \cdot 10^{-7}$	$1.4 \cdot 10^{-27}$
$1.00 \cdot 10^{-7}$	$2.80 \cdot 10^{-7}$	$1.8 \cdot 10^{-7}$	$1.3 \cdot 10^{-27}$
$6.00 \cdot 10^{-8}$	$1.90 \cdot 10^{-7}$	$1.3 \cdot 10^{-7}$	$2.8 \cdot 10^{-28}$
$1.00 \cdot 10^{-8}$	$1.50 \cdot 10^{-7}$	$1.4 \cdot 10^{-7}$	$1.7 \cdot 10^{-28}$

3.2.1. Role of impurities

The results obtained with fluoride electrode under different experimental conditions (see Table III) shows that Δc_F still remains constant thereby indicating that F^- impurities in the buffer used or in the background electrolyte do not account for the observed behaviour.

Table III

Relationship between Δc_F and c_F^a for various concentrations
of background electrolyte and buffer

The three sets of measurements were performed with the Beckman electrode at 25)

Experiment no	Background electrolyte	Buffer	Measured E' (mV)	Measured value of s (mV)
I	NaNO ₃ , 1M	CH ₃ COONa, 0.3M pH=5.5	-193.5 ± 1.2	-60.1 ± 0.3
II	NaNO ₃ , 0.1M	none pH=5.5	-195.2 ± 5.4	-59.0 ± 1.2
III	none	CH ₃ COONa, 0.1 M pH=5.5	-194.0 ± 1.8	-58.0 ± 0.4

TABLE III

RELATIONSHIP BETWEEN Δc_F AND c_F^a FOR VARIOUS CONCENTRATIONS OF BACKGROUND ELECTROLYTE AND BUFFER

Experiment I		Experiment II		Experiment III	
c_F^a (M)	Δc_F (M)	c_F^a (M)	Δc_F (M)	c_F^a (M)	Δc_F (M)
1.5 · 10 ⁻⁶	1.6 · 10 ⁻⁷	4.0 · 10 ⁻⁶	1.1 · 10 ⁻⁷	1.5 · 10 ⁻⁶	2.7 · 10 ⁻⁷
8.0 · 10 ⁻⁷	1.9 · 10 ⁻⁷	8.0 · 10 ⁻⁷	4.0 · 10 ⁻⁷	8.0 · 10 ⁻⁷	3.1 · 10 ⁻⁷
6.0 · 10 ⁻⁷	1.2 · 10 ⁻⁷	6.0 · 10 ⁻⁷	2.1 · 10 ⁻⁷	6.0 · 10 ⁻⁷	2.1 · 10 ⁻⁷
5.0 · 10 ⁻⁷	1.6 · 10 ⁻⁷	3.0 · 10 ⁻⁷	2.1 · 10 ⁻⁷	4.0 · 10 ⁻⁷	1.7 · 10 ⁻⁷
4.0 · 10 ⁻⁷	1.5 · 10 ⁻⁷	1.0 · 10 ⁻⁷	2.0 · 10 ⁻⁷	3.0 · 10 ⁻⁷	1.6 · 10 ⁻⁷
3.0 · 10 ⁻⁷	1.3 · 10 ⁻⁷			1.5 · 10 ⁻⁷	2.0 · 10 ⁻⁷
1.5 · 10 ⁻⁷	2.6 · 10 ⁻⁷			1.0 · 10 ⁻⁷	2.2 · 10 ⁻⁷
1.0 · 10 ⁻⁷	2.0 · 10 ⁻⁷				
6.0 · 10 ⁻⁸	2.4 · 10 ⁻⁷				
1.0 · 10 ⁻⁸	2.8 · 10 ⁻⁷				

3.2.2. Role of solubility of the electrode

As Δc_F varies very little with c_A^a regardless of experimental conditions, one can deduce that the solubility of the electrode membrane in the Δc_F term would be very small. This was confirmed by the fact that Δc_F remained unchanged when acetate ion concentration was varied between 0 and 0.3 M, although one would expect a variation in Δc_F due to complexation of lanthanum ions with acetate. Moreover, neutron activation measurements for lanthanum (1.1.1.) ion concentrations in fluoride solutions, after equilibration with the electrode showed that the solubility of the electrode crystal ($2-3 \times 10^{-8}$ M) is not the primary factor for the observed discrepancy. I.R. spectra of lanthanum fluoride powder pre-treated with fluoride solution as well as electrode measurements at different pH values (4 - 7) showed that hydroxide ions do not have much influence on the observed behaviour.

3.2.3. Effect of adsorption

3.2.3.1. Principle

Although the adsorption of silver and fluoride ions on the walls of the container at low concentrations have been reported (ref. 17), this can be avoided by using freshly prepared solution and clean beakers. Moreover, the reproducibility of the results shows that the adsorption or desorption of ions on the walls of the container at low concentrations is negligible. On the other hand, adsorption of ions on the crystal surface can occur and such an assumption was made by Ross (19) in the discussion of sulphide electrode. This process might also explain the "memory" effect observed with certain ion selective electrodes. Thus for the adsorption at the electrode-solution interface, a mathematical expression was derived on the basis of a Langmuir type isotherm (ref. 20). This gave :

$$\Delta c_A = c_T - c_A^a = c_A^i + KC_E + \frac{Z_M}{Z_A} \cdot \frac{K_{sp}^{1/Z_A}}{Z_A^M Z_A} \cdot \frac{1}{(c_T - KC_E)^{Z_M/Z_A}} +$$

$$+ \left[\frac{K_L (c_T^0 - KC_E)}{1 + K_L (c_T^0 - KC_E)} - \frac{K_L (c_T - KC_E)}{1 + K_L (c_T - KC_E)} \right] \cdot \frac{S \Gamma}{V} \quad (25')$$

where c_T^0 is calculated from the measured potential of the solution in which electrode is preconditioned, c_A^a is the concentration of impurities of test ion in the background electrolyte, K_{CE} is the contribution from interference of ions from background electrolytes, K_L is the adsorption equilibrium constant, S , Γ and V are surface area of the electrode, surface concentration and volume of the solution respectively.

3.2.3.2. Adsorption of fluoride on lanthanum fluoride powder

The possibility of adsorption of fluoride ions at the solid-solution interface was verified by adding different quantities of lanthanum fluoride powder to fluoride solutions of concentration c_F^a ($c_F^a = 10^{-4}$ M) and measuring the corresponding potentials with the fluoride electrode. These electrode measurements were done in the presence of the lanthanum fluoride suspension as well as after centrifuging the solution. In both cases, an increase in potential was observed indicating a decrease in fluoride concentration.

This might be ascribed to adsorption of fluoride ions by lanthanum fluoride. In addition, it was found that addition of lanthanum ions (10^{-3} - 10^{-5} M) to 10^{-5} fluoride solutions does not have any effect on potential showing that lanthanum ions do not interfere in the potential measurements.

The influence of various factors such as the weight of lanthanum fluoride (p), volume V, etc. on the adsorption was investigated. Since the surface area s of the powder is proportional to p, Δc_F should become more negative when p is large and V is small. Observations borne out the expectation. It should be pointed out that the reproducibility of the results was not good owing to the fact that the surface area of the colloidal suspension of lanthanum fluoride formed in aqueous solution is difficult to control. Further evidence of adsorption of fluoride ions on lanthanum fluoride powder was obtained from ESCA analysis.

3.2.3.3. Adsorption of fluoride on the electrode crystal

Evidence for the adsorption of fluoride on the electrode was obtained by measuring Δc_F as a function of c_F^O , keeping c_F^a constant (see Fig. 14). In these measurements, fluoride electrode was first equilibrated in fluoride solution of concentration c_F , quickly rinsed with demineralised water, dried with tissue paper and then dipped into fluoride solution of concentration c_F^a .

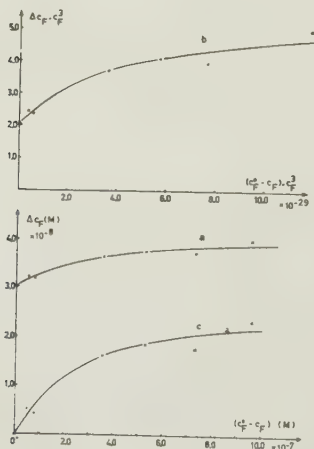


Figure 14 The relation between Δc_F and c_F^0 (curve a), $\Delta c_F \cdot (c_F^0)^3$ and $(c_F^0 - c_F)(c_F^0)^3$ (curve b), and $(c_F - K_{sp}/c_F^3)$ and c_F^0 (curve c). Results obtained with the Orion electrode in 10^{-2} M NaNO_3 without acetate buffer, $T = 25 \pm 0.1^\circ$. In curve c, the points are experimentally measured values and the continuous curve was calculated from the values of K_L and SF obtained as indicated in the text. In all these measurements, c_F^a was kept constant at 10^{-8} M.

It can be seen that (from Fig. 14) Δc_F increases with c_F^0 and the curve has a profile of an adsorption isotherm. The results with chloride electrode showed that chloride ions unlike fluoride ions are not adsorbed at the electrode surface.

Assuming $K_{CE} = 0$ and $c_A = 0$, in eq. (25) K_{sp} can be found by extrapolating the curve in Fig. 14 to $(c_F^0 - c_F) = 0$ (see eq. 25). A value of 6.7×10^{-31} was obtained for K'_{sp} . By substituting this value in eq. (), K_L and SF were estimated by means of a computer programme and values of $(3.9 \pm 1) \cdot 10^6 \text{ M}^{-1}$ and $(6.8 \pm 2.7) \times 10^{-10}$ were obtained for K and SF respectively. The value of $\Gamma = 0.64 \text{ ion A}^{-2}$ was evaluated using 0.8 CM^2 for macroscopic surface area of the crystal, using these values theoretical curve shown in Fig. 14 (curve c) was obtained.

3.2.4. Solubility of electrode crystal in different media

Solubility measurements were carried out both in the absence of background electrolyte or buffer, and in their presence (IM NaNO_3 and 0.3 M acetate ions) by the procedure described above gave results which were in accordance with that obtained with 10^{-2} M NaNO_3 for the former, but K_{sp} value (2×10^{-3} M) for the latter was found to be greater than that obtained using 10^{-2} M NaNO_3 as the background electrolyte. The high value of K'_{sp} may result from (a) decrease in activity co-efficients of lanthanum (III) and fluoride ions because of an increase in ionic strength; (b) complexation of lanthanum (III) ions with the acetate ($\alpha_{La} = 10^{1.73}$); (c) the presence of impurities or interference in the electrolyte. The precision of the measurements does not allow these three factors to be distinguished. The corrected value of K'_{sp} after taking into account α_{La} was found to be $3.7 \cdot 10^{-30}$.

Finally, the effect of complexing agent on the solubility of electrode crystal was studied. Anomalous results were obtained presumably due to

adsorption of ligands on the electrode surface or because the observed equilibrium is an apparent one.

Thus it is reasonable to conclude that the order of magnitude for solubility product of lanthanum fluoride crystal is 10^{-30} . The sensitivity of these electrodes is governed by adsorption in the case of fluoride and solubility in the case of chloride.

4. Response time of the electrode

Although some studies on the response time of ISE (21 - 23) have been made, the response mechanism of these electrodes is still not well understood. We have also attempted to study the response time of ISE in order to find out what process occurs at the solid-solution interface. An empirical equation relating potential E and time has been established and is as follows :

$$E = E_{eq} - \frac{1}{A t + B} \quad (26)$$

where A and B are constants, E is the potential corresponding to time t and E_{eq} is the equilibrium potential.

The value of E_{eq} can be obtained if potential measurements are made at various times (t) using the re-arranged form of eq. (26).

Re-arrangement of equation (26) gives :

$$\frac{(Et - E_i t_i)}{(E - E_i)} = E_{eq} \frac{(t - t_i)}{(E - E_i)} - B/A \quad \dots \quad (27)$$

where E_i and t_i are initial potential and time respectively. Thus a plot of the left and side (LHS) of the equation against $\frac{t - t_i}{E - E_i}$ should give a straight line of slope E_{eq} . Excellent straight lines were obtained for fluoride and chloride electrode. Eq. (26) appears to be applicable to other solid state electrodes e.g. Cu, Pb and Cd.

5. Application of ISE to water analysis

Finally, the fluoride electrode was applied for fluoride analysis in water. Water from different sources such as Tap water, "Sembrancher" river water, as well as "Henniez" mineral water were analysed using the addition technique and the results were found to be in agreement with the spectrophotometric results. Effect of addition of aluminium to these samples was also studied.

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